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Simulations of ZnS deposition on Ag₂S surface and formation of Ag₂S/ZnS heteronanostructure

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Abstract. Simulation of ZnS deposition from aqueous solution on a surface of crystalline Ag₂S has been performed to determine the features of formation of Ag₂S/ZnS heteronanostructures. The classical molecular dynamics and density functional theory have been used to study the features of the initial stages of ZnS growth on Ag₂S [001] surface. By classical molecular dynamics it was established that sulfur atoms initially are adsorbed on the Ag₂S. Zinc atoms were shown to be adsorbed after sulfur atoms. However, the final location of the first adsorbed Zn layer was closer to the Ag₂S surface than location of the first adsorbed S layer. Density functional theory calculation showed that Zn atoms were indeed closer to Ag₂S surface and confirmed classical molecular dynamics results. However, density functional theory results are more precise since they made possible to account for Ag₂S surface reconstruction.

1. Introduction

Semiconductor silver sulfide Ag₂S and zinc sulfide ZnS are demanded materials of modern electronics [1-4]. Modifying of electronic and optical properties of sulfides and composites of different sulfides can be reached by a change of band gap. The band gap of sulfides varies with a decrease in the size of particles and with the creation of sulfide heteronanostructures (nanocomposites) of two different metals [5]. It is known that doping of zinc sulfide by silver sulfide leads to a large decrease in the band gap. The creation of semiconductor nanocomposites consisting of Ag₂S and ZnS nanoparticles allows adjusting the band gap of Ag₂S/ZnS heteronanostructures. One of the methods for the production of heteronanostructures based on nanostructured zinc and silver sulfides is the co-deposition from aqueous colloidal solutions [6, 7].

Experimental synthesis of Ag₂S/ZnS heteronanostructures in aqueous solutions has some problems. In particular, two types of particles of Ag₂S/ZnS heteronanostructure were observed. Some particles of the heteronanostructures synthesized represent plate-like nanoparticles of silver sulfide, which consist from disoriented crystal blocks with the sizes from 2 to 5 nm. Particles of silver sulfide are covered partially by thinner lamellar nanoparticles of cubic zinc sulfide. Ag₂S/ZnS heteronanostructures of the second type are core-shell type nanoparticles. The core of these nanoparticles consists of silver sulfide and has a size 10-30 nm. Ag₂S core is covered by ZnS shell with a thickness about 4-5 nm.



The sequence of deposition of atoms of a different type (Zn or S) on silver sulfide is not quite clear. Possibility of deposition of silver sulfide on ZnS is not clear too.

The features of the formation of the Ag₂S/ZnS heteronanostructure in an aqueous solution can be found by simulations.

The main task of mathematical modeling of nanostructures is to predict their properties. There is still no single method for modeling nanostructures. This is primarily due to the limited capabilities of computer technology because the most accurate first-principle calculations based on quantum mechanics [8] do not allow modeling large arrays of atoms. Therefore, the classical molecular dynamics (CMD) method based on Newtonian mechanics is used for this purpose [9, 10].

In the present work, the process of capture of ions of zinc and sulfur by Ag₂S surface has been simulated using the molecular dynamics. Since in CMD simulation Ag₂S layers were frozen, the reconstruction of its surface wasn't accounted for. For considering the surface reconstruction, density functional theory simulation was performed. The main objective of simulation was to determine the features of formation of the first ZnS layer on Ag₂S [001] surface.

2. Simulations Details

Classical molecular dynamics simulation was performed by means of LAMMPS software [11] (<http://lammps.sandia.gov>) using a model with implicit solvent. It means that solvent molecules are not simulated, and their effect is accounted for by applying random force to dissolved atoms. Thus, in the simulated system only four types of atoms are presented: Ag and S from Ag₂S and dissolved Zn and S. Figure 1 represents the initial configuration of the simulation. For Ag and S atoms of Ag₂S surface the equations of motion are not solved, thus, these atoms don't change their positions with time, thus Ag₂S surface is "frozen". For Zn and S atoms from the solution the equations of motion are presented by Langevin equation [12]:

$$m\mathbf{a} = -\frac{\mathbf{v}}{b} - \nabla U + \mathbf{F}_L, \quad (1)$$

where m is the mass of the particle; \mathbf{a} and \mathbf{v} are the acceleration and speed of a particle; b is mobility of the particle; U is the potential energy of the particle due to the interaction with other particles and external field; \mathbf{F}_L is Langevin force (which replaces the effect of solvent molecules).

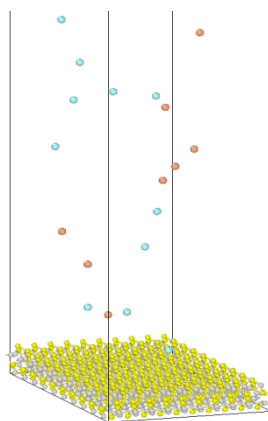


Figure 1. Initial configuration of CMD simulation

Types of interaction for CMD simulations between different types of atoms are presented in the Table 1. There is no interaction between pairs of frozen atoms. The detailed description of Tersoff potential can be found elsewhere [13]. For all Lennard-Jones interactions the cut-off distance is equal to corresponding σ parameter, thus, only repulsion is described by Lennard-Jones interactions. For fixing of adsorbed sulfur atom three Ag-S bonds are required, thus, 3 different sets of parameters are

presented in Table 1 for the pair Ag-S_{sol}. These parameters were found from the “energy-volume” dependence of Ag₂S unit cell obtained by density functional theory calculation.

Table 1. Interaction between different atom types in the system

Pair of atoms	Type of interaction	Parameters
S _{Ag2S} -Zn S _{sol} -Zn	Tersoff potential	$A=2475.8$ eV $B=225.5$ eV $\gamma = 1$ $\lambda_1 = 3.0099$ Å ⁻¹ $\lambda_2 = 1.7322$ Å ⁻¹ $\lambda_3 = 0$ $\beta = 1.1 \cdot 10^{-6}$ $m = 3$ $n = 0.78734$ $c = 100390$ $d = 16.217$ $\cos\theta_0 = -0.59825$ $R = 3.059$ Å $D = 0.15$ Å
S _{Ag2S} -S _{sol} S _{sol} -S _{sol}	Lennard-Jones potential*	$\varepsilon = 0.01538$ eV $\sigma = 3.85$ Å
Ag-Zn	Lennard-Jones potential	$\varepsilon = 0.01295$ eV $\sigma = 3.11$ Å
Ag-S _{sol}	Parabolic function**	$r_{01} = 2.593$ Å $k_1 = 6.432$ eV·Å ⁻² $r_{02} = 2.664$ Å $k_2 = 6.901$ eV·Å ⁻² $r_{03} = 3.047$ Å $k_3 = 4.658$ eV·Å ⁻²

$$* U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

$$** E = (k/2)(r - r_0)^2.$$

For accounting of features of Ag₂S surface reconstruction and more physical description of ZnS unit deposition on Ag₂S surface density functional theory (DFT) simulations were performed using VASP software [14]. The cut-off energy for plane wave basis set was chosen to be 450 eV. For bulk calculations 7x7x7 Monkhorst-Pack [15] grid was used, and for [001] surface calculation 7x7x1 grid was used. Perdew-Burke-Ernzerhof [16] pseudopotentials were used for all calculations.

First, the energy of 1x1x3 unreconstructed slab was computed (E_{slab}^{ur}). Then, the atoms in two neighboring cells were allowed to change their positions until each component of force acting on them become lower than 10⁻² eV/Å. The minimization of forces was performed using conjugate gradient algorithm [17]. Obtained reconstructed structure had the energy E_{slab}^r . Surface reconstruction energy was computed as

$$E_r^{001} = (E_{slab}^r - E_{slab}^{ur})/ab, \quad (2)$$

where a and b are lattice parameters of Ag₂S (4.2264 Å and 6.9282 Å respectively). It should be mentioned that the absence of factor 2 in denominator of (2) is connected with the fact that only one of two surfaces of a slab was allowed to relax.

For obtaining S and Zn positions the following steps were performed. First, a sulfur atom was placed at not reconstructed Ag₂S surface at its “ideal” position (the position which would this sulfur atom occupy in perfect infinite crystal). After that, structural relaxation was performed keeping atoms

in the bottom unit cell frozen. Then, Zn atom was added to this relaxed 3 Ag₂S+S system. The initial position of Zn atom was calculated as follows

$$\mathbf{r}_{\text{Zn}} = \frac{\mathbf{r}_{\text{S1}} + \mathbf{r}_{\text{S2}}}{2} + \frac{[(\mathbf{r}_{\text{S2}} - \mathbf{r}_{\text{S1}}) \times (\mathbf{r}_{\text{S2}} - \mathbf{r}_{\text{S1}}) \times \mathbf{k}]}{||(\mathbf{r}_{\text{S2}} - \mathbf{r}_{\text{S1}}) \times (\mathbf{r}_{\text{S2}} - \mathbf{r}_{\text{S1}}) \times \mathbf{k}||} \cdot \sqrt{d_{\text{ZnS}}^2 - (\mathbf{r}_{\text{S2}} - \mathbf{r}_{\text{S1}})^2/4}, \quad (3)$$

where $\mathbf{r}_{\text{S1,2}}$ are the positions of two sulfur atoms closest to the surface, \mathbf{k} is {001} vector, d_{ZnS} is the smallest distance between zinc and sulfur in cubic ZnS, $[\mathbf{a} \times \mathbf{b}]$ means cross product of \mathbf{a} and \mathbf{b} .

For computing adsorption energy of ZnS unit, energies of single Zn and single S atoms were calculated. Then, the adsorption energy was computed as follows

$$E_{\text{ads}} = E_{\text{Ag}_2\text{S}+\text{ZnS}} - (E_{\text{S}} + E_{\text{Zn}} + E_{\text{slab}}^r), \quad (4)$$

where $E_{\text{Ag}_2\text{S}+\text{ZnS}}$ is the energy of relaxed 1x1x3 Ag₂S + ZnS structure.

3. Results and Discussion

3.1 Classical MD simulation

A model with the following approximations was used for the final calculation of ZnS deposition on the Ag₂S surface: (1) Ag₂S is represented by a plate having a thickness of one unit cell and containing 15×15 surface cells of silver sulfide; (2) above each Ag₂S unit cell, zinc and sulfur atoms are located one at a time randomly in planes which are parallel to the Ag₂S surface, and are at a distance of 10 Å from each other; (3) the initial speed of zinc and sulfur atoms was the same, directed perpendicular to the Ag₂S surface and equal to $4.1 \cdot 10^{-3}$ Å·fs⁻¹; (4) every 10000 machine steps or every 10 ps, forces directed perpendicularly downwards to the Ag₂S surface and equal to 0.043 and 0.086 eV·Å⁻¹, were applied to the sulfur and zinc atoms, respectively; (5) to eliminate the high deposition speed, which can be caused by the periodic application of these forces, the Nose-Hoover algorithm was used for constant temperature 300 K molecular dynamics simulations. All these approximations are aimed to imitate Ag₂S surface in very diluted ZnS solution.

In this calculation, it is important to find out what positions are occupied by the atoms of sulfur and zinc on the surface of Ag₂S.

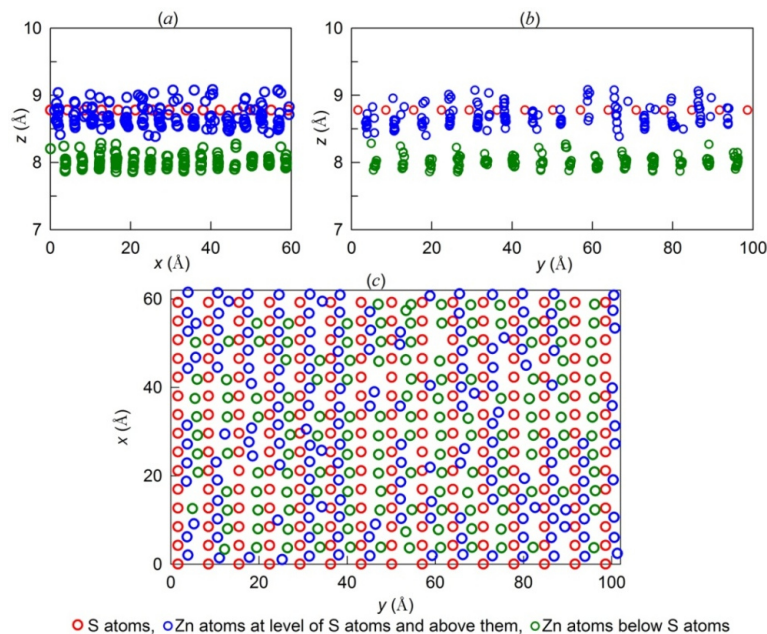


Figure 2. Projections of the positions of Zn and S atoms that are situated above the Ag₂S surface on the (a) [x0z], (b) [0yz], and (c) [xy0] planes.

The positions of S atoms on the surface of Ag_2S are indirectly set in advance because Ag-S bonds make the position of S atoms unambiguous. The calculated projections of the positions of Zn atoms that are situated over the Ag_2S surface and averaged over time are shown in Figure 2. The projections of the positions of surface S atoms on the $[xy0]$ plane are presented in Fig. 2c. In fact, these are the positions around which the deposited sulfur atoms should oscillate.

For CMD calculations mean distance between atoms in the closest to the surface Zn layer (green circles on Fig. 2) and sulfur atoms (red circles on Fig. 2) is 3.07 Å which significantly differs from the smallest Zn-S distance in cubic ZnS ($d_{\text{ZnS}} = 2.34$ Å).

3.2 Density functional theory calculation

The energy of $1 \times 1 \times 3$ unreconstructed slab obtained by DFT calculations is equal to $E_{\text{slab}}^{\text{nr}} = -113.059$ eV, and the energy of $1 \times 1 \times 3$ reconstructed slab to $E_{\text{slab}}^{\text{r}} = -114.163$ eV. Thus, reconstruction energy was estimated according to (2) to be -0.038 eV/Å² or -0.603 J·m⁻². Energy of final relaxed $1 \times 1 \times 3$ $\text{Ag}_2\text{S} + \text{ZnS}$ structure is $E_{\text{Ag}_2\text{S}+\text{ZnS}} = -120.389$ eV, and energies of single Zn and S atoms are $E_{\text{Zn}} = -0.011$ eV and $E_{\text{S}} = -0.875$ eV, respectively. According to (4), the adsorption energy of ZnS unit on $[001]$ Ag_2S surface is 5.34 eV.

The structural changes of Ag_2S surface + ZnS are presented in Figure 3.

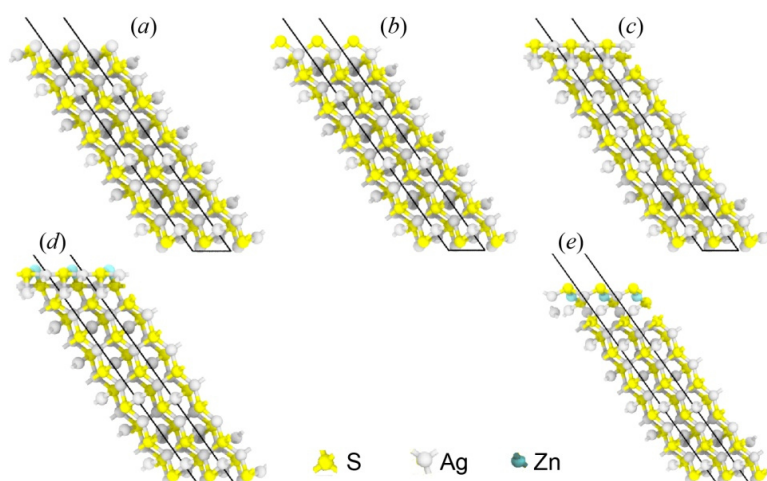


Figure 3. Structure of Ag_2S $[001]$ surface with adsorbed ZnS: (a) pure unreconstructed Ag_2S surface; (b) unreconstructed Ag_2S surface with additional sulfur atom, i. e. $\text{Ag}_2\text{S}+\text{S}$ system; (c) relaxed $\text{Ag}_2\text{S}+\text{S}$ system; (d) relaxed $\text{Ag}_2\text{S}+\text{S}$ system with Zn atom placed according eq.(4); (e) relaxed $\text{Ag}_2\text{S}+\text{S}+\text{Zn}$ system.

From Fig. 3 we observe that Zn atoms are indeed closer to Ag_2S surface than adsorbed S atoms, which agrees with CMD simulations. But the distance between Zn and S atoms in this case equals 2.16 Å, which is much closer to Zn-S distance in cubic ZnS comparing to CMD study. Moreover, downward difference is reasonable, as far as there are no attractive forces acting atoms from vacuum, which makes the bond lengths shorter comparing to bond lengths in bulk material.

4. Conclusions

CMD simulations of ZnS deposition on Ag_2S surface demonstrated, that sulfur atoms are first deposited from the solution. However, in spite of the fact that Zn atoms are deposited after S atoms, positions of Zn atoms are closer to the Ag_2S surface.

Density functional theory simulation demonstrated severe relaxation of Ag_2S surface which is characterized by relatively high relaxation energy. However, structural relaxation of ZnS unit on the $[001]$ Ag_2S surface demonstrated the same tendency as CMD simulation – Zn atom was located closer to the Ag_2S surface than S atom. Zn-S distance in CMD simulations significantly differs from this one

in cubic ZnS, while for DFT simulations reasonable small downward difference is observed. This indicates, that CMD simulation could be used for ZnS deposition on Ag₂S only quantitatively but not qualitatively. However, DFT simulations has low performance and using DFT for direct modeling of described deposition is demanding to computer recourses and time. Thus, future work will be aimed for constructing of classical interatomic potential for the system Ag-S-Zn based on *ab initio* data, as far as such potential would allow to perform accurate simulation of dynamics of Zn-S deposition on Ag₂S surface due to combining accuracy of DFT and performance of CMD.

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